Supramolecular Based Sensor for the Detection of Surfactant, Adenosine Phosphate and DNA and Utilization of Urea Phosphate for the Synthesis of Glycoluril Derivatives

A SYNOPSIS

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1. INTRODUCTION

Supramolecular chemistry plays a major role in biological systems using non-covalent interactions, which was established by the Nobel Prize winners Jean-Marie Lehn, Donald J Cram, and Charles J Pedersen in 1987 [1]. Unlike the conventional phenomena of bond making and bond braking, supramolecular complex formation and dissociation of complex are dynamic and spontaneous; which are mainly based on the molecular recognition phenomena and controlled by the weaker forces of supramolecular chemistry [2]. Many of the molecular sensors that are developed have the capacity to visualize the molecular recognition phenomena through the change in color or fluorescence of the sensing materials [3]. Recent years, molecular sensors have gained much attention due to their facile preparation and high sensitivity. Despite the technical advancements in chemistry and instruments, the development of low-cost molecular sensors for many practical applications is still challenging [4]. In this thesis work, various fluorescent molecules served as a sensor to detect surfactants, DNA and adenosine phosphates such as AMP, ADP and ATP. The principle behind the development of the sensors for surfactant, DNA and adenosine phosphates is based on the competitive binding mechanism between the chosen analytes and the dye loaded on the nano-materials such as graphene oxide and copper nanoparticles. Based on this analogy, several other sensors can be developed by employing appropriate dye molecules loaded on suitable nano materials. The advantage of this new approach provides a facile preparation of sensor materials by simple mixing of the dye and the nano-materials in the presence of a reducing agent. Here, the dye switch “off” its fluorescence upon binding with metal nanoparticles or graphene materials, and subsequently the dye molecule will be released spontaneously and switch “on” its fluorescence upon interaction with the chosen analytes. The schematic representation of the thesis work is given in the Figure 1.

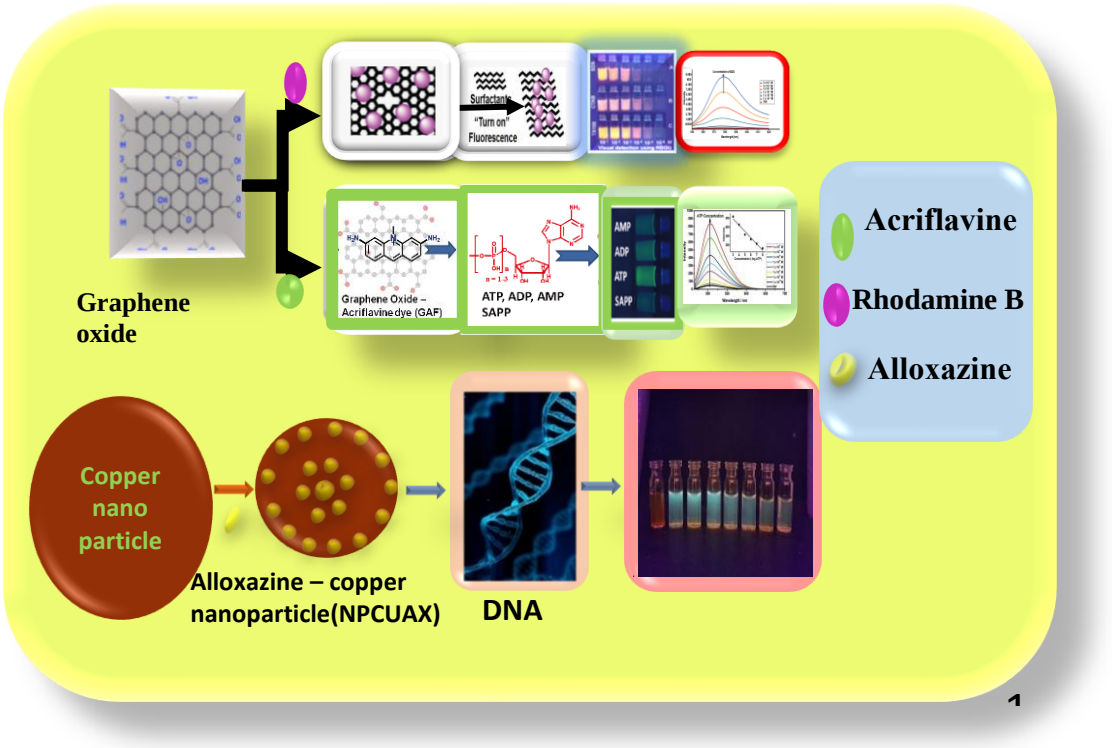

Figure 1: Supramolecular based sensors developed for the detection of surfactant, DNA and Adenosine phosphates.

The success of the above mentioned work relies on both the selection of dye and the nano-materials. Mutual compatibility is very essential for the development of a successful sensor. For example, strong interaction between dye and the nano-material often unable to release the dye upon interaction with the chosen analytes. Similarly, weak interaction between dye and the anchoring source leads to withering of dye before the interaction with the analytes. Therefore, compatibility between dye and the binding source is very crucial for the development of a good sensor.

The fluorescence dye sensor is by far the method most often applied and is the dominant analytical approach in a large variety of schemes in the fields of medical testing, biotechnology and drug discovery [5], [6]. It is also used for the detection of heavy metal ions in aqueous media [7]. Rhodamine has been broadly used in many research fields, such as the lasing medium in dye lasers and fluorescent indicators in biological studies [8], [9]. Acriflavine HCl is a type of dye commonly used as a topical antiseptic for skin infections. The monomer of this dye is widely used in analytical regents for sensing [10], and luminescence sensors [11], among several others.

Among the various dye anchoring sources, graphene oxide nanosheets can be conveniently used to load the fluorescent dyes, because carbon materials have the high affinity towards dye molecules. Dye loaded graphene materials can serve as sensor through competitive binding with the analytes and that will allow the release of loaded dye based on the binding affinity of the analytes [12]–[14]. Graphene oxide, copper nanoparticles, and several other nanomaterials have been exposed as sensors for biomarkers and biologically essential analytes. Metal nanoparticles have excellent chemical and physical properties and also a quantum size effect and a high aspect ratio, so they have attracted much more attention over recent years. The fluorescence properties of metal nanoparticles, which can be used for catalysis, sensors, and bio-labeling, must be studied for practical applications [15], [16]. High fluorescent nanomaterial provides a good fluorescent probe and it is used in various fields for the detection of metal cations and anions, DNA, protein bio-imaging and other small molecules.

Surfactants are very attractive material, because it has been consumed in large scale by the world wide population. Thus creating of a sensor for surfactant will help not only for the environmentalist but also for biochemical scientist as they use surfactants for the extraction of proteins by lysis of the cells. Until now, the reported sensors responded for surfactants of either cationic/ anionic/non-ionic surfactant. For example, a poly (3,4 propylene dioxythiophene) derivative works for both cationic and non-ionic surfactants [17]. Similarly, a potentiometric sensor was developed for both anionic and non-ionic surfactants. Furthermore, these methods are not simple to implement, because they require expensive and difficult preparation methodologies. However, rhodamine B (RhB)-anchored reduced graphene oxide (RBGO) was successfully explored and reported here as a sensor material for the detection of all types of surfactants. Besides, the present sensor material can selectively recognize anionic surfactants in the presence of copper sulfate.

ATP, ADP, and AMP become inevitable since these molecules play vital roles in cellular mechanisms and communications. Adenosine Triphosphate (ATP) is the primary energy carrier in all living organisms on earth. Among them, ATP and ADP have gained much attention, because they have been involved in many of the energy transfer steps of cellular activities. Several sensor materials for ATP have been reported in the literature; however, they often require extensive synthesis. Therefore,

development of low-cost, facile and sensitive sensors remains a challenging task. For the first time, acriflavine has been utilized for the sensing of adenosine phosphates such as ATP, ADP and AMP through anchoring on the graphene source. Among them, ATP has showed excellent fluorescence turn-on property with the highest LOD of 0.8 x 10^{-10} M. Thus, this supramolecular approach may help many future applications especially in the field of molecular sensors. Sensitive DNA detection is extremely important in clinical diagnostics, gene therapy and a variety of biomedical studies. Until now, detection of dsDNA is mainly based on the fluorophore-labeled ssDNA and the detection occurred through the formation of complementary dsDNA. Here, the combination of copper nanoparticles with alloxazine helped to detect the dsDNA through the competitive binding of DNA with copper nanoparticle, resulted in the release of fluorescence dye. By this method, detection of 50 ppm DNA was achieved which is far less than expected.

Glycolurils (2,4,6,8-tetraazabicyclo[3.3.0] octane-3,7-diones) or its derivatives have received a great attention for their practical applications such as fertilizer, catalysts, bleaching activators, radio-iodination agents for biomolecules, and as a monomer in Cucurbituril chemistry [18]. Until now, glycolurils or its derivatives have been synthesized from diketones and urea using acid/base catalyst. For the first time urea phosphate has been used to prepare glycouril and its derivatives without addition of acid/base catalyst, which greatly improved the yields of glycolurils. Besides urea phosphate has been demonstrated in the Biginelli reaction with no catalyst.

2. REVIEW OF LITERATURE

In the literature survey, sensor for anionic surfactants has been developed by dye-based strategies [19], ion-selective electrode [20], Gas chromatography (GC) [21]. Similarly, to detect cationic surfactants methods such as ion-sensitive field-effect transistor (ISFET) devices, spectrofluorimetry have been employed [22,23].

Anthracene derivatives have been explored for the detection of triphosphate nucleotides [24]. Furthermore, Zn(II) based colorimetric sensor for ATP has been established [25]. Similarly, gold nanoparticle based colorimetric sensor for the detection of mercury ions and hemoglobin has been reported [26,27]. A few fluorescent and colorimetric sensors method also reported for the detection of biomolecule [28]. Recently, some of the supramolecular assemblies developed by the combination of graphene oxide and fluorescent dyes assisted to develop sensors for

cucurbit[*n*]urils (CB[*n*], *n* = 5 – 8) [29].

Glycolurils are building blocks for many interesting host molecules such as cucurbiturils, hemicucurbiturils, bambusurils. Generally, glycoluril and substituted glycolurils have been prepared from urea and 1,2-diketones using an acid catalyst (sulfuric acid, hydrochloric acid, formic acid, acetic acid, trifluoroacetic acid) or a strong base such as potassium hydroxide [30,31].

3. OBJECTIVES

1. To use a Rhodamine B-anchored graphene oxide nanomaterial as a sensor for all types of surfactants in an aqueous medium, including ionic, non-ionic, and cationic surfactants.
2. To develop the supramolecular assembly of acriflavine for the sensing of adenosine phosphate molecules such as ATP, ADP, and AMP.
3. To develop the Alloxazine copper nanoparticles-based sensor for DNA biomolecule.
4. To synthesize glycoluril derivative compounds without the use of acid or other catalysts by using urea phosphate.
5. To perform structural characterization of synthesized sensor probes and compound materials using various instrumental techniques such as Fourier transform infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Particle Size Analyzer (DLS), powdered X-Ray Diffraction (p-XRD), NMR (Nuclear Magnetic Resonance spectroscopy), and Raman spectroscopy.
6. To study the surfactant and adenosine phosphate concentration with the help of fluorescence spectroscopy and UV-Visible spectroscopy and synthesized compounds were confirmed by NMR and Carbon-13 spectroscopy.

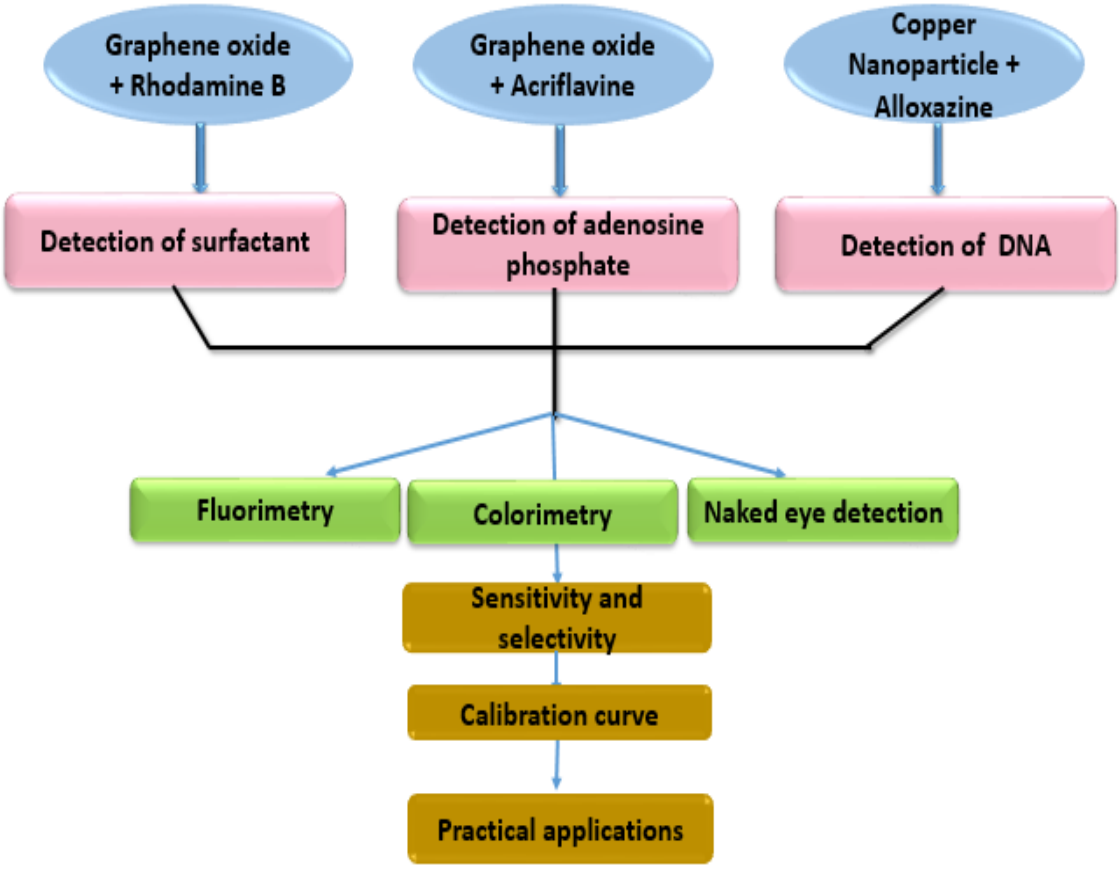

Figure 2: Flowchart representing the different stages of research work.

4. RESEARCH PROBLEM

Through the literature survey, it was found that graphene oxide, copper nanoparticle and several other carbon nanomaterials have been exposed as sensors for biomarkers and biologically essential analytes. Many sensors have been reported for either anionic or cationic surfactants or non-ionic surfactants. Until now, only a few solitary sensor materials have been reported for both ionic and non-ionic surfactants.

This thesis deals with the development of supramoleculer based sensors for detection of surfactant, adenosine phosphate and DNA. It included the development of sensors for all types of surfactant (anionic, cationic, nonionic) and biologically essential compounds such as Adenosine Phosphates and DNA (Figure 2). Besides, these sensors are facile and low-cost techniques that can be conveniently prepared and utilized for the chosen analytes. Furthermore, utilization of urea phosphate has been demonstrated for the synthesis of glycoluril and derivatives without any catalyst.

5. ORGANIZATION OF THESIS

The thesis entitled "Supramolecular Based Sensor for the Detection of Surfactant, Adenosine phosphate and DNA and Utilization of Urea Phosphate for the Synthesis of Glycoluril Derivatives". The thesis is containing eight chapters.

Chapter - I: Introduction

Various applications of supramolecular chemistry sensors are described in Chapter I, followed by nanoparticle graphene oxide fluorescence dye-based sensors and their applications. A fluorescent dye such as Rhodamine B and Acriflavine fluorescence dyes is used in many sensing applications, such as in biomolecule labelling and in chemosensor systems for detecting chemical compounds with a great variety of fluorescent dyes available, the Rhodamine dye family has an important place, and compared to other dyes, Rhodamine exhibits excellent photostability and photophysical properties. Synthesis of Alloxazine and its interaction with DNA has been accounted. The importance of glycolurils in supramolecular chemistry has been discussed. The overall characteristics of fluorescent sensors for detecting biomolecules as well as their real-time applications are discussed in Chapter I.

Chapter - II: Literature survey

An overview of the literature on nanoparticles with fluorescence dye sensors is presented in Chapter II. A variety of literature reports have been reviewed for detecting different types of surfactants and biomolecules using metal nanoparticles and organic dyes based on nanomaterial fluorescent chemosensors for metal cations, anions, and bio macromolecules. As well as investigating alternative methods for detecting surfactants and adenosine phosphate, the methods previously used for detecting surfactants and adenosine phosphate were reviewed. Several glycoluril derivatives were synthesized and their applications in supramolecular chemistry were reviewed.

Chapter - III: Experimental materials and methods

The purpose of this chapter is to describe the materials that was purchased and applied in the synthesis of nanomaterials, such as copper nanoparticles and graphene oxide nanosheets. The preparation of sensor probes such as reduced graphene oxide binding non-covalently with Rhodamine B and acriflavine by reduction method has been discussed in this part. Analytes such as surfactant, and adenosine phosphate have been analytically measured and calibrated using UV-Visible spectrophotometers and

fluorescence spectrophotometers in this chapter. Sensor probes have been tested through material characterization, such as FTIR and XRD assessments of dye-nanoparticle interactions. Using SEM, TEM, and DLS, morphology and particle size distribution were detected. By using NMR and mass spectroscopy, the synthesized glycoluril derivatives were confirmed.

Chapter - IV: A Graphene Oxide/ Rhodamine B-Based Fluorescent Sensor for All type of Surfactants

Surfactant fluorescent sensors based on graphene oxide are discussed in this Chapter. Many sensors have been reported for either anionic or cationic surfactants or non-ionic surfactants. Until now, only a few solitary sensor materials have been reported for both ionic and non-ionic surfactants. Therefore, Rhodamine B (RhB)-anchored reduced graphene oxide (RBGO) has been explored for sensing of all types of surfactants (Figure3). RBGO responded to these surfactants down to the lowest concentration of 10^{-6} M. The concentrations of the surfactants were measured by the quantitative release of RhB from the graphene materials with respect to the quantity of the surfactants present in the solution.

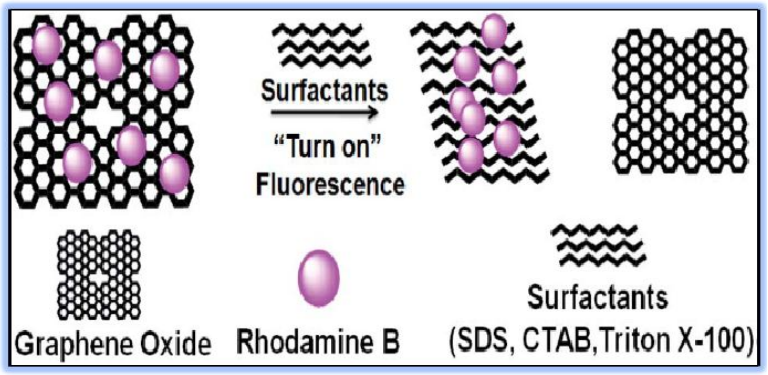

Figure 3: Fluorescent sensor of surfactants (anionic, cationic and non-ionic).

Furthermore, we also demonstrated a visual detection method for the ionic and non-ionic surfactants using the RBGO complex, which helped to visualize the surfactants under a UV (365 nm) source conveniently, and this might help to visualize the surfactants at any location easily. Therefore, this facile supramolecular assembly of RBGO can be a good complementary tool for the detection of surfactants from environmental samples.

Chapter - V: A Graphene Oxide/Acriflavine Based Fluorescence Sensor for Adenosine Phosphate Detection

Adenosine phosphate detection sensor based on Graphene oxide/Acriflavine deliberated in this chapter. An acriflavine-graphene oxide (GAF) supramolecular assembly has been prepared from water-soluble graphene oxide (GO) and a fluorescent dye, acriflavine (AF). Upon binding this non-covalently to the GO, the fluorescence of acriflavine has been "turned off" effectively, competitive binding potential of the sensor substrates such as ATP, ADP, AMP and the pyrophosphate weakens the supramolecular assembly of GAF, which allows the release of acriflavine quantitatively, which also "turns-on" the fluorescence of the dye under UV irradiation (Figure 4). Interestingly, GAF displayed the highest sensitivity towards ATP within the family of adenosine phosphates. It provides opportunity to develop a naked eye detection method for the adenosine phosphates biomolecules. For the first time, acriflavine has been utilized for the sensing of adenosine phosphates in combination with GO, which can be useful for the detection of other biomolecules.

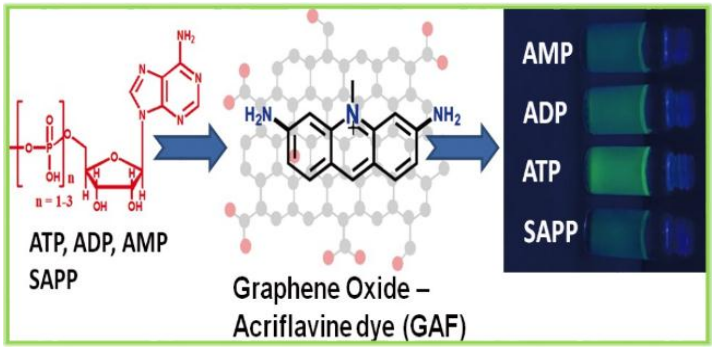

Figure 4: Acriflavine-graphene oxide supramolecular assembly (GAF) for the detection of Adenosine Phosphates such as ATP, ADP and AMP

Chapter – VI: Alloxazine - Copper Nanoparticles-Based Fluorescence Sensor for DNA Detection

Fluorescent methods have gained much attention and have been broadly applied for the detection of various biomolecules. In this Chapter, we developed a highly selective and sensitive fluorescence sensing approach for DNA detection based on Alloxazine-copper nanoparticle supramolecular assembly. The Alloxazine-copper nanoparticle "turn on" the fluorescence upon interaction with DNA solutions (Figure 5). The combination of copper nanoparticles with alloxazine helped to detect the dsDNA through the competitive binding of DNA with that of the dye loaded in the copper nanoparticle resulted in the release of fluorescence dye. By this method

detection of 50 ppm DNA was achieved which is far less than expected. Furthermore, a naked eye detection method for the DNA biomolecules has been established.

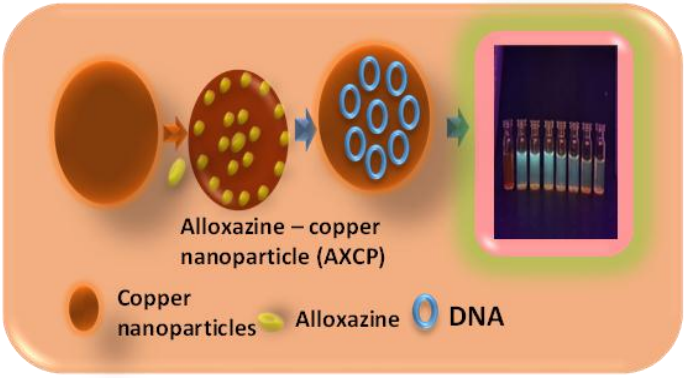

Figure 5: Alloxazine-Copper Nanoparticles Supramolecular Assembly for the detection of DNA.

Chapter - VII: Synthesis of Glycoluril Derivatives using Urea Phosphate

This chapter deals with synthesis of Glycoluril using Urea Phosphate. Glycolurils are building blocks for the synthesis of cucurbiturils that are important host materials for several applications. Glycolurils are prepared conveniently by the condensation of 1,2-diketones with urea using an acid/base as catalyst.

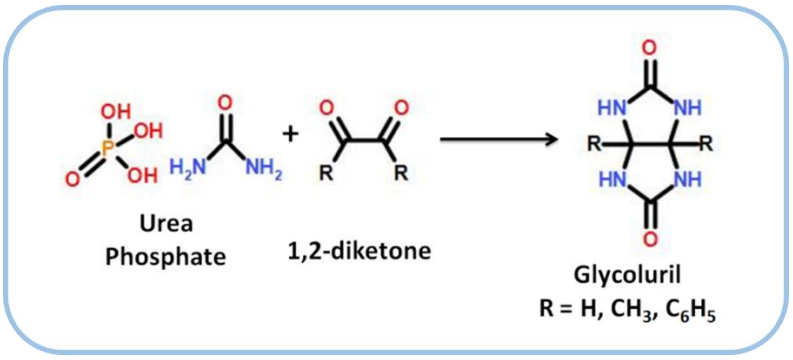

Figure 6: Synthesis of glycoluril using urea phosphate

Here, we reported a facile method of synthesis of various glycolurils using urea phosphate and 1,2-diketones. The scheme of this work is represented in the figure 6. The proposed procedure is advantageous due to mild conditions, simple operations, no need of using other catalysts and minimized side reactions. The results suggest that urea phosphate can be considered as the best substitute for urea in many organic reactions where acid catalysis is required. In a similar way, Biginelli synthesis of 3,4-dihydropyrimidin-2-ones has been carried out using urea phosphate, acetylacetone and benzaldehyde (Figure 7).

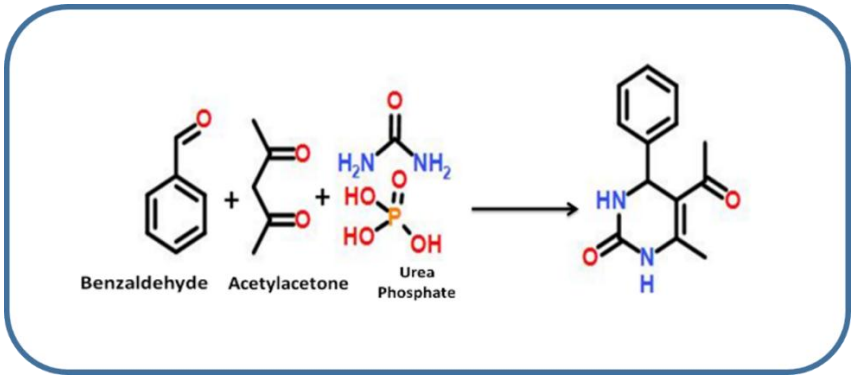

Figure 7: Synthesis of 3,4-dihydropyrimidin-2-one by Biginelli synthesis

Chapter - VIII: – Summary and Conclusion

In summary, a novel technique for the detection of surfactant and biomolecules such as adenosine phosphate and DNA has been developed using graphene oxide and copper nanoparticle tethered with fluorescent dyes. A facile, simple and low-cost detection method for the surfactants of ionic and non-ionic types was successfully demonstrated using RBGO. This new method of determination will complement other existing methods in many ways. It showed the importance of RBGO in the determination of anionic, cationic and non-ionic surfactants. The sensitivity of this method for all the surfactants was achieved as low as 10^{-6} M in water. Unlike other colorimetric procedures, no organic solvent was involved in the detection procedure and thus, the procedure required minimum efforts and also, it demonstrated a naked eye detection method for all the surfactants under a UV light, which helped visualize the surfactants at the minimum concentrations of $10^{-3}$and 10^{-4} M for non-ionic and ionic surfactants, respectively. For example, instead of adding expensive ELSD to HPLC for the detection of surfactants, the addition of RBGO may support the HPLC detection method in a more facile and efficient way.

Similarly, a facile method to prepare supramolecular assemblies of graphene oxide with acriflavine has been extablished. For the first time, acriflavine has been utilized for the sensing of adenosine phosphates in combination with GO, which can be useful for the detection of other biomolecules. GAF has displayed good selectivity towards ATP compared with other adenosine phosphate moieties and the sensitivity of GAF towards ATP exists at nanomolar concentrations, which is on par with other reported methods. GAF displayed the highest sensitivity towards ATP within the family of adenosine phosphates. This allowed developing a naked eye detection method for the adenosine phosphate biomolecules under UV light. Thus, GAF may be

useful for fluorescence cell imaging and for measuring ATP at nanomolar concentrations in biological systems. Additionally, copper nanoparticle-alloxazine based sensor for DNA was developed and developed a naked eye detection method for the DNA biomolecules under UV light. The sensitivity of this method for DNA was achieved as low as 50ppm in water.

Besides, a new synthetic protocol has been developed for the synthesis of glycoluril and its derivatives from urea phosphate and 1,2-diketones. Glycolurils are building blocks for many interesting host molecules such as cucurbiturils, hemicucurbiturils, bambusurils and many others. The proposed procedure is advantageous due to mild conditions, simple operations, no need of using other catalysts and minimized side reactions. The utility of urea phosphate has also been demonstrated by the Biginelli synthesis of pyrimidinone derivative. Further study on the use of urea phosphate in various organic reactions is in progress.

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